

Table 2:

Ex.	p [bar]	T [°C]	H ₂ [l (STP/h)]	MA conversion [bar]	BDO [%]	GBL [%]	THF [%]	BuOH [%]	SA/SAN [%]	Carbon balance [bar]
5	80	160	50	100	91.4	0.7	0.1	4.4	0	98.3
6	90	150	25	100	91.1	1.8	0.3	6.6	0	101.9

Comparative example 2: Catalyst C2

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658 g of ZrO₂ extrudates (XZ 16509 from Norton Process Prod. Corp., Akron (OH), USA, 82 m²/g, pore volume 0.28 cm³/g) were coated with a mixture of 27.3 g of Re₂O₇ and 131.3 g of platinum nitrate solution (16% by weight of Pt) in 90 ml of water. The material was mixed thoroughly until the commencement of drying and subsequently dried at 120°C for 16 h.

10 Afterwards, the material was reduced in a reduction column at 270°C in a mixture of 10 l (STP)/h of hydrogen and 50 l (STP)/h of nitrogen for 8 h, cooled in the reaction mixture and conditioned in water under flowing nitrogen. The catalyst contained 2.7% by weight of Re and 2.4% by weight of platinum.

15 Comparative example 3

25 ml of catalyst C2 were crushed to 0.1 - 1 mm spall and installed into a continuous tubular reactor. The feed consisted of a maleic acid solution (10% of maleic acid) and was metered in at 25 g/h. 50 l (STP)/h of hydrogen were added. The reaction conditions are 160°C and 80 bar. The liquid effluent was analyzed by means of gas chromatography. The values in table 4 are each quoted as yields in % per mole of maleic acid.

Table 4:

Ex.	MA conversion [bar]	BDO [%]	GBL [%]	THF [%]	BuOH [%]	SA/SAN [%]	Carbon balance [bar]
C3	100	19.7	0.0	20.3	0.1	0	41.3

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Comparative example 4: Catalyst C4

ZrO₂ extrudates (XZ 16509 from Norton Process Prod. Corp., Akron (OH), USA, 82 m²/g, pore volume 0.28 cm³/g) was crushed to 1.2 - 2 mm spall. 200 g of the support were coated with

39.24 g of a platinum nitrate solution (16.25% by weight of Pt) which had been diluted with water beforehand to 160 ml. After a contact time of 3 h, the material was dried at 100°C and a pressure of 30 - 50 mbar for 2 h. Afterwards, the material was heated to 150°C under 200 l (STP)/h of N₂ over 30 min and kept at this temperature for 60 min, and a mixture of 100 l (STP)/h of H₂ and 100 l (STP)/h of N₂ were subsequently fed in at this temperature for 60 min, the material was heated to 300°C within 30 min and the conditions were maintained for a further 3 h. The precatalyst was then cooled to 50°C in this reducing atmosphere and subsequently in pure N₂ (200 l (STP)/h) to room temperature. The material obtained was passivated with a mixture of 10 l (STP)/h of O₂ in 180 l (STP)/h of N₂ over 14 h. In the next step, this precatalyst was coated with 40 ml of an aqueous solution of Re₂O₇ (10% by weight of Re₂O₇) with the addition of a further 140 ml of water. The contact time was 3 h. Afterwards, the material was dried at 100°C and a pressure of 30 - 50 mbar over 2 h. The finished catalyst was reduced in the same manner as the precatalyst. The catalyst contained 2.9% by weight of Re and 2.5% by weight of Pt.

15 Comparative example 5

25 ml of catalyst C4 were installed into a continuous tubular reactor. The feed consisted of a maleic acid solution (10% of maleic acid) and was metered in at 25 g/h. 50 l (STP)/h of hydrogen were added. Hydrogenation was effected at 160°C and 80 bar. The liquid effluent was analyzed by means of gas chromatography. The values in table 5 are each quoted as yields in % per mole of maleic acid.

Table 5

Ex.	MA conversion [bar]	BDO [%]	GBL [%]	THF [%]	BuOH [%]	SA/SAN [%]	Carbon balance [bar]
C5	100	15.3	46.6	20.3	0.2	22.2	107.7

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Example 7: Catalyst D

658 g of ZrO₂ extrudates (XZ 16509 from Norton Process Prod. Corp., Akron (OH), USA, 82 m²/g, pore volume 0.28 cm³/g) were coated with stirring with 27.3 g of Re₂O₇ in 180 ml of water. The mixture was dried at 120°C and afterwards heated to 150°C under 200 l (STP)/h of N₂ over 30 min and kept at this temperature for 60 min. Subsequently, a mixture of 100 l (STP)/h of H₂ and 100 l (STP)/h of N₂ was fed in for 60 min, the material was heated to 300°C within 30 min and these conditions were maintained for a further 3 h. The precatalyst was then cooled to 50°C in this reducing atmosphere and subsequently in pure N₂ (200 l (STP)/h) to room

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temperature. Finally, the material was passivated with a mixture of 10 l (STP)/h of oxygen in 180 l (STP)/h of N₂ over 14 h. In the next step, 131.3 g of a platinum nitrate solution (16% by weight of Pt) were diluted with 70 ml of water and the precatalyst was saturated with stirring with this solution. After drying at 120°C for 16 h, the finished catalyst was reduced in the same way as the precatalyst. The catalyst contained 2.8% by weight of Re and 2.9% by weight of Pt.

Example 8

25 ml of catalyst D were comminuted to 0.1 - 1 mm spall and installed into a continuous tubular reactor. The feed consisted of a maleic acid solution (10% by weight of maleic acid) and was metered in at 25 g/h. 50 l (STP)/h of hydrogen were added. Hydrogenation was effected at 140°C and 80 bar. The liquid effluent was analyzed by means of gas chromatography. The values in Table 6 are each quoted as yields in % per mole of maleic acid.

Table 6

Ex.	MA conversion [bar]	BDO [%]	GBL [%]	THF [%]	BuOH [%]	SA/SAN [%]	Carbon balance [bar]
8	100	87.9	0.0	0.0	3.1	0.0	91.5

Example 9: Catalyst E

8.2 kg of TiO₂ powder (Degussa P25 from Degussa AG, Düsseldorf, 39 m²/g) were admixed with dilute formic acid (47.1 g of 85% HCOOH in 1350 g of water) and kneaded in a pan grinder with the addition of 2.86 kg of water for 2 h. The finished composition was forced through a die at 25 - 60 bar in an extruder, so that extrudates of thickness 4.5 mm were formed. The extrudates were dried at 120°C for 16 h and then calcined initially at 470°C for 140 min and finally at 500°C for 3 h. 8 g of Re₂O₇ in 360 ml of water were added in a rotary evaporator to 200 g of the TiO₂ support crushed to 0.1 - 1 mm spall and, after a contact time of 15 min, the catalyst precursor was dried at 100°C and 10 mbar for 2 h. The material was heated to 300°C in a rotary furnace under 50 l (STP)/h of N₂ and heat-treated for 1 h. Subsequently, an additional 10 l (STP)/h of hydrogen for 1.5 h and 25 l (STP)/h of hydrogen for a further 2 hours were added to the nitrogen. The catalyst precursor was cooled under N₂ and passivated with a mixture of 5 l (STP)/h of air in 100 l (STP)/h of N₂ at room temperature overnight for further processing. Subsequently, a batch of 37.5 g of a platinum nitrate solution (16% by weight of Pt) was diluted with 320 ml of water and added to the catalyst precursor. After a contact time of 15 min, drying was effected at 100°C and 10 mbar for 2 h. The material was heated to 300°C in a rotary

furnace under 50 l (STP)/h of N₂ and heat-treated for 1 h. Subsequently, an additional 10 l (STP)/h of hydrogen for 1.5 h and 25 l (STP)/h of hydrogen for a further 2 hours were added to the nitrogen. The catalyst was cooled under N₂ and conditioned in water under flowing nitrogen. The finished catalyst contained 2.4% by weight of platinum and 2.9% by weight of rhenium.

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Example 10

12 ml of catalyst E were installed into an autoclave together with 80 ml of aqueous maleic acid solution (5% by weight of maleic acid). Hydrogen was injected to 75 bar at room temperature.

10 The temperature was increased to 160°C. After 1 h, the reaction was terminated. The liquid effluent was analyzed by means of gas chromatography. The values in table 7 are each quoted as yields in % per mole of maleic acid.

Table 7

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Ex.	MA conversion [bar]	BDO [%]	GBL [%]	THF [%]	BuOH [%]	SA/SAN [%]	Carbon balance [bar]
10	100	60.1	0.1	1.1	19.8	0.0	85.1

Example 11: Catalyst F

For pretreatment, 2000 ml of the activated carbon support (Eco Sorb BG09, spall from F.A.W.

20 Jacobi AB, Stockholm, Sweden) were boiled to reflux with 3800 g of 41% phosphoric acid for 40 h. After cooling, the material is washed with water until a pH of 5 has been attained. The activated carbon is finally dried at 120°C for 14 h. 150 g of the support were coated with stirring with 150 ml of an aqueous solution of 15.2 g of Re₂O₇ and dried at 120°C for 16 h. Afterwards, the material was heated to 150°C under 200 l (STP)/h of N₂ over 30 min and kept at this

25 temperature for 60 min, then a mixture of 100 l (STP)/h of H₂ and 100 l (STP)/h of N₂ was fed in for 60 min, and the material was heated at 300°C within 30 min and the conditions were maintained for a further 3 h. The precatalyst was then cooled to 50°C in this reducing atmosphere and subsequently cooled down to room temperature in pure N₂ (200 l (STP)/h).

Finally, the material was passivated with a mixture of 10 l (STP)/h of oxygen in 180 l (STP)/h of

30 N₂ over 14 h for further processing. In the next step, 31.3 g of a platinum nitrate solution (16% by weight of Pt) were diluted with 120 ml of water and the precatalyst was saturated with stirring with the solution. Afterwards, the material was dried at 120°C for 16 h. The finished catalyst was reduced in the same way as the precatalyst. The precatalyst contained 6.8% by weight of rhenium and 2.8% by weight of platinum.

Comparative example 6: Catalyst C6

150 g of the support from example 13 were saturated with stirring with 31.3 g of a platinum
 5 nitrate solution (16% by weight of Pt) diluted with 120 ml of water. Afterwards, the material was
 dried at 120°C for 16 h and heated to 150°C under 200 l (STP)/h of N₂ and maintained at this
 temperature for 60 min. Subsequently, a mixture of 100 l (STP)/h of H₂ and 100 l (STP)/h of N₂
 was fed in for 60 min, the material was heated to 300°C over 30 min and the conditions were
 maintained for a further 3 h. The precatalyst was then cooled to 50°C in this reducing
 10 atmosphere and subsequently down to room temperature in pure N₂ (200 l (STP)/h). Finally, the
 material was passivated with a mixture of 10 l (STP)/h of oxygen in 180 l (STP)/h of N₂ over
 14 h. In the next step, the material precoated with platinum was saturated with stirring with
 150 ml of an aqueous solution of 15.2 g of Re₂O₇ and dried at 120°C for 16 h. The finished
 catalyst was reduced in the same way as the precatalyst. The catalyst contained 6.5% by weight
 15 of rhenium and 2.7% by weight of platinum.

Examples 12 and 13, comparative example 7

25 ml of catalyst in each case were installed into a continuous tubular reactor. The feed
 20 consisted of an aqueous maleic acid solution (10% by weight of maleic acid). 50 l (STP)/h of
 hydrogen were added. The liquid effluent was analyzed by means of gas chromatography. The
 values in table 8 are each quoted as yields in % per mole of maleic acid.

Table 8:

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Ex.	Cat.	p [bar]	T [°C]	Feed [g/h]	MA conversion [%]	BDO [%]	GBL [%]	THF [%]	BuOH [%]	SA/SAN [%]	Carbon balance [%]
12	F	80	160	25	94.9	93.1	1.1	0.5	4.0	0.0	105.2
13	F	80	180	37.5	86.4	73.3	6.0	1.0	3.4	0.0	98.2
C7	C6	80	160	25	89.9	34.5	55.1	0.1	0.6	17.8	118.3

Example 14

25 ml of catalyst A were installed into a tubular reactor to be operated continuously. The feed
 30 consisted of a 10% by weight aqueous maleic acid solution and was metered in at 25 g/h. The
 catalyst was started up with this solution. Hydrogenation was effected with 50 l (STP)/h of
 hydrogen at 160°C and 80 bar. The liquid reaction effluent was analyzed for its 1,4-butanediol

PF 54043

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content by means of gas chromatography after different reaction times and plotted in graph 1 against time.

Example 15

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The hydrogenation was carried out in a similar manner to example 16, except that the catalyst was started up using pure water for 12 h. Maleic acid solution and hydrogen were then metered in. The 1,4-butanediol contents determined were included in graph 1 as a second graph.